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OF CRITICAL-FLUID EXTRACTIONS IN THE PROCESS
INDUSTRIES

Final Report

April 1982

Work Performed Under Contract No. AI01-81CS66001

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ASSESSMENT OF CRITICAL-FLUID EXTRACTIONS
IN THE PROCESS INDUSTRIES

Final Report

to

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Jet Propulsion Laboratory
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by

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April, 1982

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I. SUMMARY AND CONCLUSIONS

This report presents an assessment of the potential for critical-fluid extraction as a separation process for improving the productive use of energy in the process industries. Critical-fluid extraction involves the use of fluids, normally gaseous at ambient conditions, as extraction solvents at temperatures and pressures around the critical point. Equilibrium and kinetic properties in this regime are very favorable for solvent applications, and generally allow major reductions in the energy requirements for separating and purifying chemical components of a mixture.

A review of public information plus interviews with industry and academic participants in the field led to the identification of a series of candidate applications for the technology. This list was narrowed to those which appear to have the highest potential for more productive energy use. These include:

1. Recovery of oxygenated organics from water, plus other distillation substitutes:
 - (a) Water-oxygenated organics alone (current distillation energy): impact on the order of 0.1 quad per year.
 - (b) Favorable growth of fuel ethanol, or proliferation to petroleum refining distillations: impact on the order of 1.0 quad per year.
2. Residual oil supercritical extraction, current asphalt production: impact on the order of 0.2 quad per year.
3. Vegetable oil extraction, current production: impact on the order of 0.01 quad per year.

A series of recommendations are outlined for long-range research and development to provide initial momentum for commercial use and further development. Priorities among these include:

1. Applications data on real systems.
2. Studies of transport phenomena and unit operations.
3. Thermodynamic data.
4. Chemical reactions.

The results of the assessment clearly showed that a substantial potential for improved productive use of energy in process industries could be realized with introduction of critical-fluid extraction technology. Because the field is relatively unexplored, it would benefit greatly at this stage if these research and development priorities were initiated. Such R&D could be highly productive, and important in stimulating follow-up development under private industrial sponsorship.

II. PROGRAM OBJECTIVES AND APPROACH

Critical Fluid Systems, Inc. was asked by Jet Propulsion Laboratory (JPL) to carry out an assessment of the potential for critical-fluid extractions as a separation process for improving productive use of energy in the process industries. The study was carried out as part of a larger effort undertaken by JPL for the U.S. Department of Energy in evaluating new technologies in the process industries and their energy-productivity impact, and to provide recommendations for long-term research and development. The subcontract statement of work is attached in Appendix A.

The program objectives were:

1. To obtain a list of candidate applications for critical-fluid extractions which would have a high-payoff potential for improving energy productivity;
2. To make a preliminary estimate of the energy savings potential for successful use of the technology in the candidate applications;
3. To define long-term research and development needed.

The approach taken was to review appropriate sources of non-proprietary information, including the public literature, on fundamentals and applications of critical-fluid extraction technology. As part of that review, two major conferences were attended, each of which involved focused symposia in the field. Also, a series of interviews was carried out with industrial groups interested in using or offering the technology, and academic groups performing related research. A list of interviewees is given in Appendix B.

Section III of this report provides a brief overview of the fundamental characteristics of critical-fluid extraction, with emphasis on the unique properties of fluid systems that are used to advantage in the technology. Also described is the impact of these process characteristics on the potential for improved energy productivity.

In Section IV, the list of high-payoff potential candidate applications is described, plus the criteria used to narrow these to provide appropriate candidates.

In Section V, estimates are presented for the energy-productivity potential for the candidate applications. These estimates, while preliminary, take into account the current energy requirements of production as now practiced, and the production volumes involved.

In Section VI, an outline of long-term research and development needs is presented.

III. THE TECHNOLOGY

A. Fundamentals

The use of near-critical and supercritical fluids as extractants has been of interest to a number of groups for at least 20 years. Successful applications rest on the economic gain that more than offsets the cost of high-pressure operation. An important component of that gain is improved productivity per unit of energy input. Fundamental properties of critical fluids which ultimately lead to such process advantages are reviewed in this section.

The thermodynamic critical temperature is the highest temperature at which two fluid phases (liquid and gas) of a pure substance can coexist. Similarly, the critical pressure is the highest pressure at which two fluid phases of a pure substance can coexist. Table I lists the critical properties for a number of fluids which have been proposed for extraction processes. Processes which employ a fluid at conditions of temperature and pressure greater than the critical values are called, variously: gas-extraction, dense-gas-extraction, and supercritical extraction.

The supercritical fluid (SCF) region can best be visualized with the aid of a reduced pressure-density diagram, shown in Figure 1. The dashed curve is the locus of liquid-vapor equilibrium, which terminates at the critical point (C.P.). The reduced density of the normal liquid is about 2.6: in other words, the critical density is about 40% of that of the normal liquid.

The SCF region refers to reduced temperatures in the range of 1 to about 1.4 and reduced pressures from 1 to about 6; the near-critical (NCL) state refers to the region bounded by $.95 < T_r < 1$. In the SCF and NCL regions, fluids still have high enough densities to exhibit liquid-like solubility behavior, yet the densities are low enough so that transport properties are appreciably higher than those of normal liquids.

Studies with solvents such as carbon dioxide, ethylene, and ethane have been reported by a number of investigators (1,2,3). As shown in Table 1, these three are of interest because they fall in the near-supercritical regime at ambient temperatures, with critical pressures in the range of 50 to 75 atmospheres. In this regime, liquid-like solvent properties are demonstrated, as shown in Figure 2, for naphthalene in CO_2 (4). This diagram is based on published solubility data in the near-supercritical region (3), plus the solubility of naphthalene in saturated liquid CO_2 (5). From these data, two interaction parameters have been derived as required for the Peng-Robinson modification of the Redlich-Kwong equation of state (6), at present the best correlation basis near the critical point.

TABLE I
CRITICAL PROPERTIES FOR SELECTED FLUIDS

<u>Fluid</u>	<u>T_c, °C</u>	<u>P_c, atm</u>	<u>ρ_c, g/cm³</u>
ethane	32.3	48.8	0.203
propane	96.9	42.6	0.220
butane	152.0	38.0	0.228
pentane	296.7	33.8	0.232
ethylene	9.9	51.2	0.227
ammonia	132.4	112.8	0.235
carbon dioxide	31.1	73.8	0.468
sulfur dioxide	157.6	78.8	0.525
water	374.3	221.1	0.326

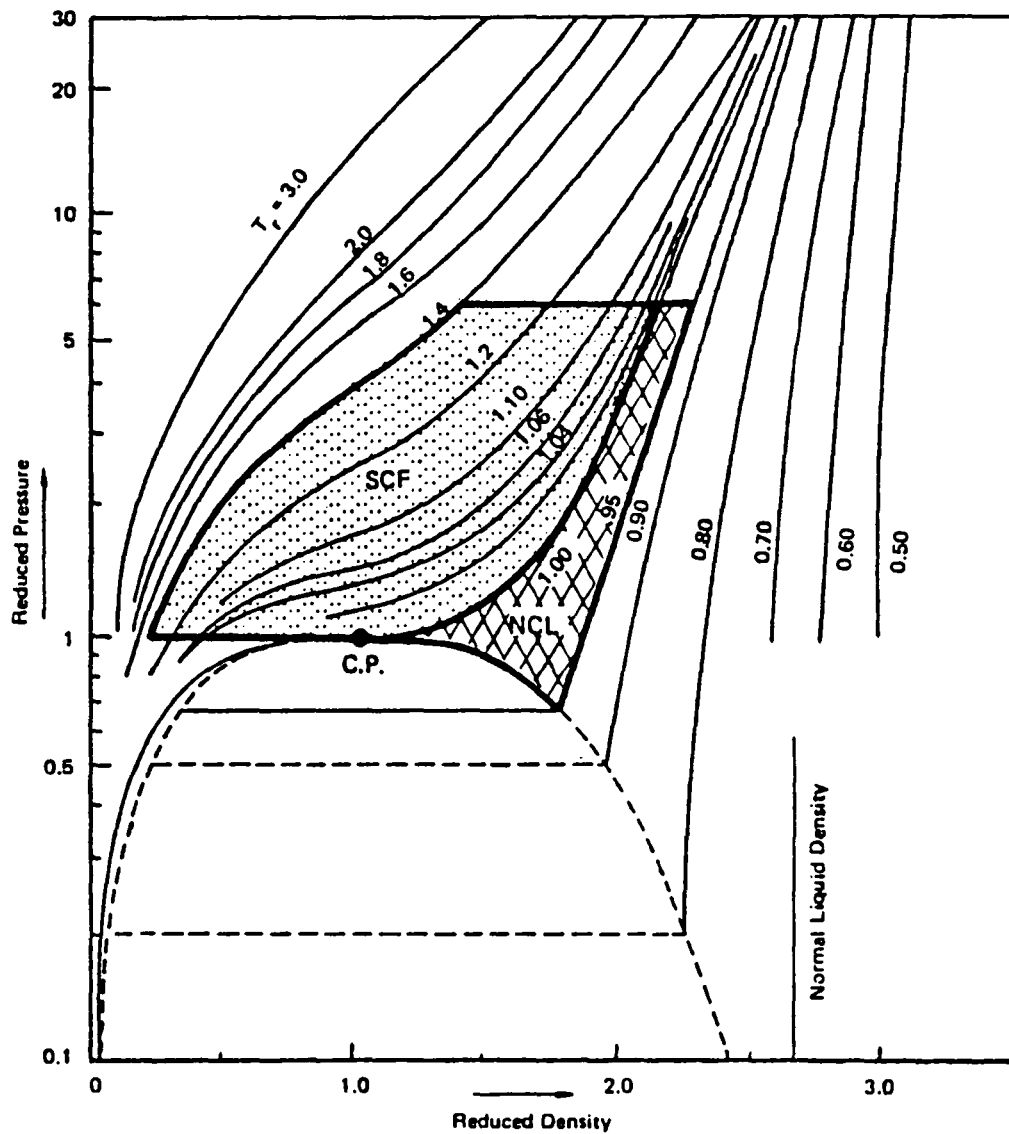


FIGURE 1. REDUCED PRESSURE-DENSITY DIAGRAM. SUPERCRITICAL FLUID (SCF) AND NEAR-CRITICAL LIQUID (NCL) REGIONS, AS INDICATED

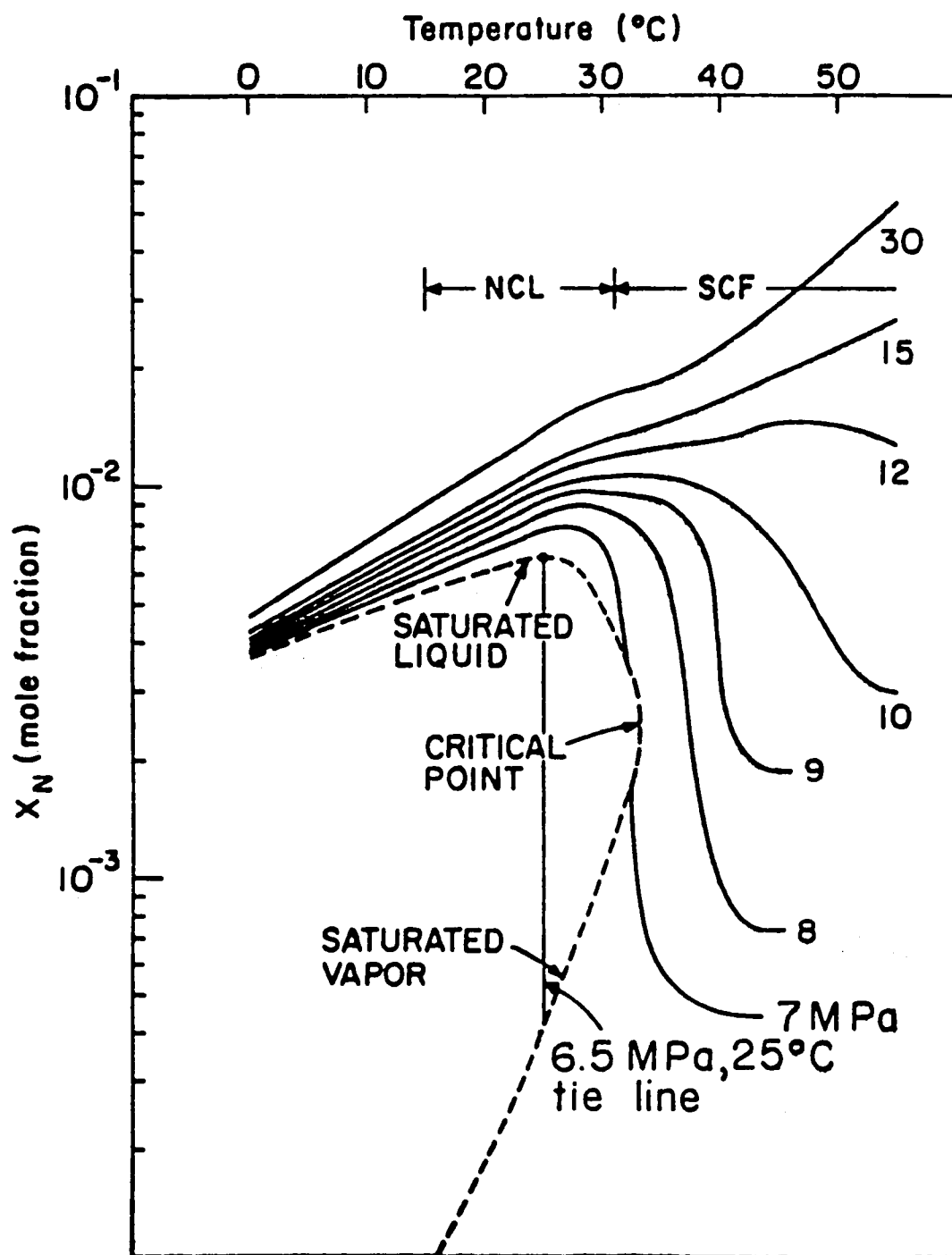


FIGURE 2. SOLUBILITY MAP OF NAPHTHALENE IN SCF AND NCL CARBON DIOXIDE

Several characteristics of this plot are of interest, and they serve to describe solubility behavior in solvents near the critical point in general. At pressures above 150 atmospheres, the solubility behavior is essentially an extension of that typically observed in the liquid phase: naphthalene solubility increases with increasing temperature, and there is a relatively small effect of increasing pressure. At temperatures above the critical but at pressures below about 80 atmospheres, the "solution" is gas-phase, and the "solubility" of solute is controlled mainly by its vapor pressure. In the intermediate pressure region at supercritical temperatures within 50° of the critical, there is a mixture of gas-like and liquid-like behavior. Among other phenomena, inversions of solubility trends with temperature at constant pressure are common. The general form of this solubility map is common to all partly-miscible solutes near the critical point of the solvent. The naphthalene-CO₂ data give a good indication of the very large enhancement in solubility that has been observed in solvents that would normally be considered gases, when those solvents are in the near-critical or supercritical state.

Although there are scant data in the literature on solubilities of organic solids and liquids in supercritical fluids, there is a large body of data on solubilities in near-critical liquids. For example, Francis (5) reported the mutual solubilities of NCL CO₂ at 25°C with each of 261 organic substances. Each of these solubilities represents a single data point on a solubility map. For example, Francis reports the solubility of naphthalene in liquid CO₂ at 25°C as 2 weight-percent. In Figure 2, the corresponding point lies on the saturated liquid curve at 25°C, which is 0.62 mole-percent or about 2 weight-percent. Thus, Francis' data can be used as a guide for the magnitude of solubility in the critical region. It should be noted that nearly half of the compounds studied by Francis were completely miscible with NCL CO₂. The naphthalene solubility behavior discussed above is representative of the less soluble organics in CO₂.

It is evident from Figure 2 that solubility at high pressure (150-300 atm) and supercritical temperature can be substantially higher than the solubility in saturated liquid at 25°C. At some point of higher pressures and temperatures, solutes that are only slightly soluble at 25°C will become completely miscible. That is, the system of solute + solvent reaches a mixture critical point beyond which only a single, homogeneous phase exists. Such critical loci have been reported for a number of organics with CO₂ (7). The pressure-temperature projections of the critical loci for mixtures of CO₂ and several alkanes are shown in Figure 3 (8). For octane, for example, there exists a continuous vapor-liquid critical locus connecting the critical points of the pure materials. There is also a liquid-liquid critical locus that exists at low temperatures. To the right of the L-L critical and above the L-G critical, only one phase exists; in that region, octane and CO₂ are completely miscible. For tridecane and higher molecular weight alkanes, the L-G and L-L critical loci merge into a single, continuous

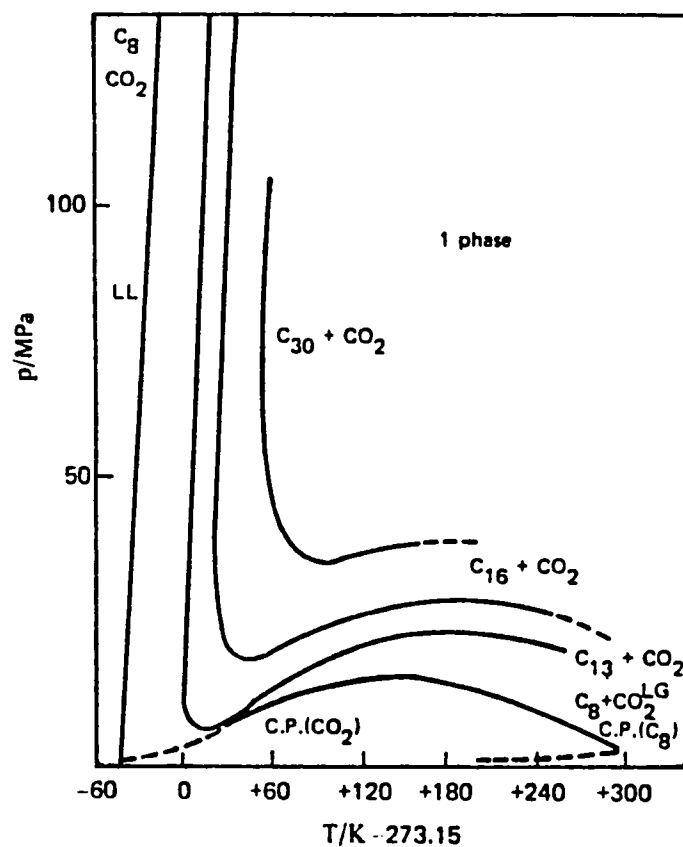


FIGURE 3.

P-T PROJECTIONS OF THE PHASE DIAGRAMS AND CRITICAL LOCI OF BINARY CO₂ + ALKANE MIXTURES. FULL LINES, CRITICAL CURVES; DASHED LINES, VAPOR PRESSURE CURVES OF CARBON DIOXIDE AND OCTANE, RESPECTIVELY.

critical locus. To the upper right side of the critical locus, the system is completely miscible; below it and to the left, the system exhibits two or more phases of limited miscibility.

This brief discussion of solubility phenomena in the critical region illustrates several important generalizations:

1. Enhanced solubility in the critical region is a general phenomenon exhibited by any solute.
2. A large number and variety of organic compounds are partially or completely miscible with CO₂ in the near-critical liquid region.
3. Partially miscible systems at near-critical liquid conditions tend toward complete miscibility at supercritical conditions.

In addition to high solubility, a good extracting agent should exhibit high diffusivity for rapid mass transfer. There is relatively little direct data on diffusivities in supercritical fluids, but there is a growing body of indirect evidence showing rapid mass transfer.

Several investigators have measured self-diffusivity of CO₂ in the sub- and supercritical region⁽⁹⁾. These data have been correlated to develop a map of self-diffusivity as given in Figure 4. In liquid CO₂ at 25°C, the diffusivity is about an order-of-magnitude higher than that of conventional liquid solvents. The vapor diffusivity at 25°C is higher by another factor of 10. At supercritical temperatures, the diffusivities vary between 10⁻³ and 10⁻⁴ cm²/sec, decreasing from the higher to lower values with increasing density. By comparison of Figures 2 and 4, it can be seen that the decrease in diffusivity with density is less than the increase in solubility with density: at 40°C, the diffusivity decreases from 80 atm (8 x 10⁻⁴ cm²/sec) to 120 atm (1.5 x 10⁻⁴) by a factor of 5.3, while the solubility increases from 80 atm (0.1 mole-percent) to 120 atm (1.2 mole-percent) by a factor of 12. Thus, the gain in solubility at higher density more than outweighs the decrease in diffusivity.

Further evidence of favorable transport properties come from viscosity of CO₂ around the critical point. Figure 5 gives viscosity data in the temperature and pressure range of interest⁽¹⁰⁾. Values are on the order of 0.04-0.08 centipoises, about a factor of 10 to 20 lower than those of normal liquids.

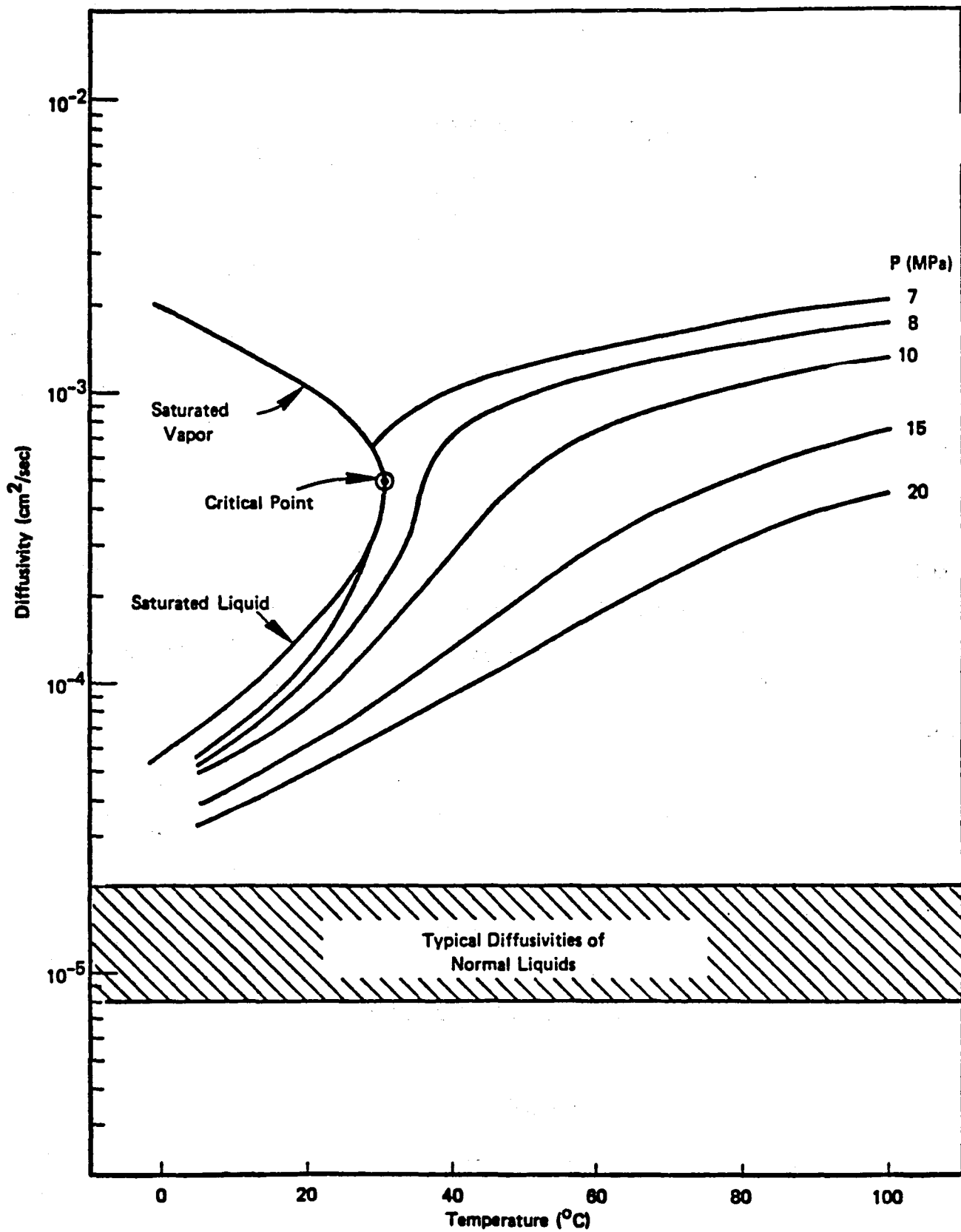
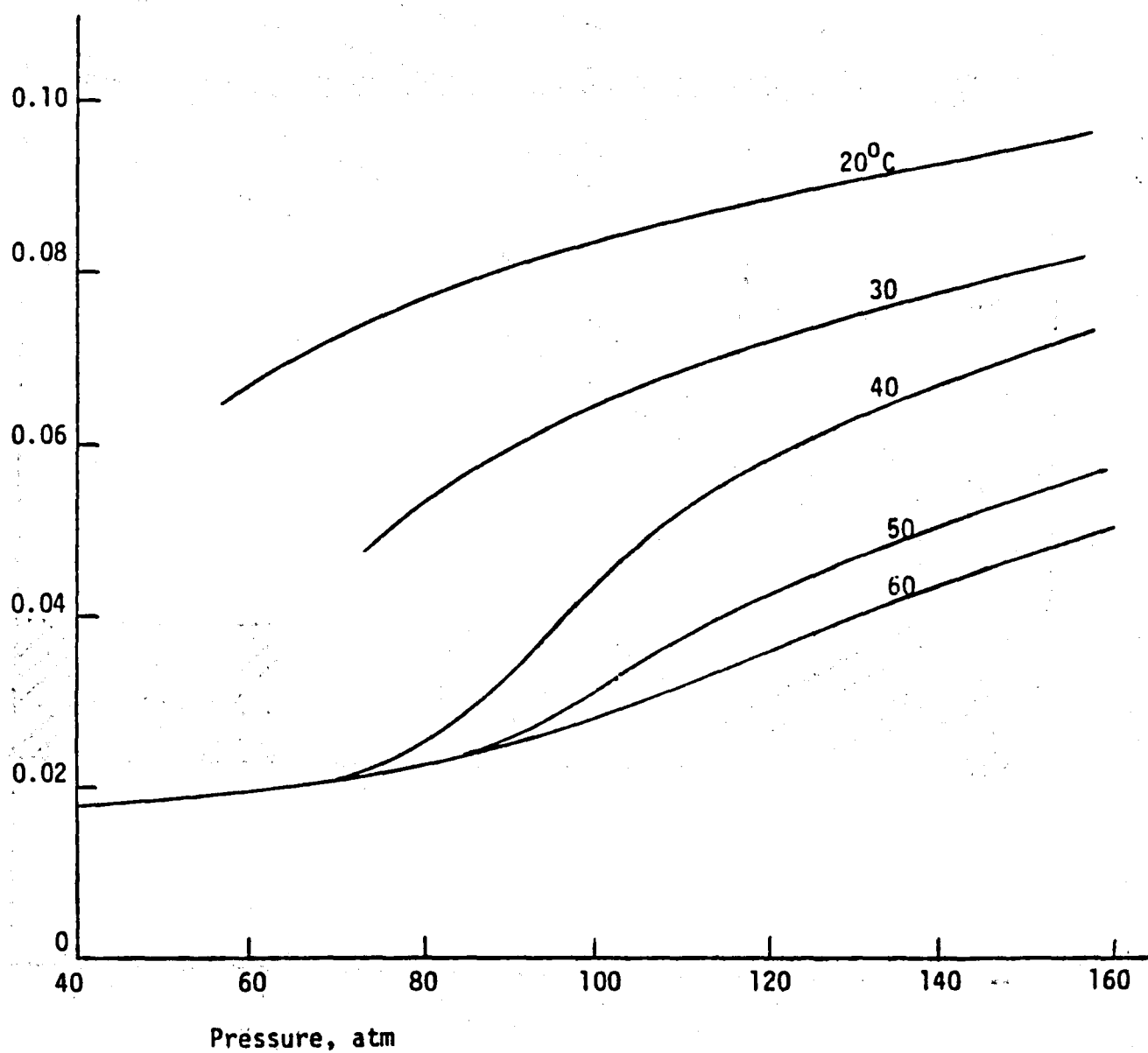


FIGURE 4. DIFFUSIVITY OF CARBON DIOXIDE IN THE SCF AND NCL REGIONS

FIGURE 5

VISCOSITY OF CARBON DIOXIDE



Certain unusual thermophysical properties of fluids near the critical point have implications in process engineering. The latent heat of vaporization at the critical point is zero, because of the disappearance of the phase transition. As saturation temperature-pressure conditions for vapor-liquid equilibrium approach the critical point, the heat of vaporization decreases rapidly; this change is illustrated in Table 2 (11), showing the latent heat for carbon dioxide near its critical point. At 0°F (-17.8°C), the value is about 120 btu/lb; at 70°F (21.1°C), it is about half, 64 btu/lb.

A second anomalous aspect of thermophysical behavior is related to heat capacity in the supercritical regime (12). At temperatures about 15-20°C above the critical, heat capacities are unusually high, several-fold higher than the liquid value. At 1-2°C above the critical, the heat capacity is about an order-of-magnitude higher than the corresponding liquid value.

B. Impact of Critical-Fluid Properties on Higher-Productivity Use of Energy

At the current time, several companies are offering processes or have processes in advanced development which incorporate the use of critical-fluid extraction. Process details are proprietary, so complete information on process operation is unavailable. However, some generalizations may be made which serve to demonstrate the use of unique properties of critical fluids in providing more productive use of energy than major established separation processes.

It appears that the flow schematic of a critical-fluid extraction process will follow one of two basic designs. In the first general case, recovery of product from critical-fluid solvent occurs by changing temperature and/or pressure conditions to permit solute precipitation, with no phase change of the solvent. In the second general case, solute separation occurs by vaporization of the solvent.

The first case is illustrated in Figure 6. Critical-fluid solvent is recirculated, by means of a pump or compressor, flowing through an extraction vessel under temperature and pressure conditions where solubility of the extractable solute is favorable. The extract solution flowing from the extractor undergoes a pressure or temperature change, which causes a substantial change in the solubility of extracted solute in the solvent, much as naphthalene solubility is shown to change in CO₂ in Figure 2. The solute phase separates from the fluid solvent, removed in a two-phase separator, and the solvent is brought back to high-solubility conditions for recirculation to the extractor.

TABLE 2

HEAT OF VAPORIZATION
OF CARBON DIOXIDE

<u>Temperature</u>		<u>Saturation Pressure</u>	<u>Heat of Vaporization</u>
<u>°F</u>	<u>°C</u>	<u>atm</u>	<u>btu/lb</u>
0	-17.8	20.8	120.1
40	4.4	38.6	95.0
60	15.6	50.9	76.6
70	21.1	58.1	63.8
80	26.7	65.9	44.8
87.8	31.0	72.7	0

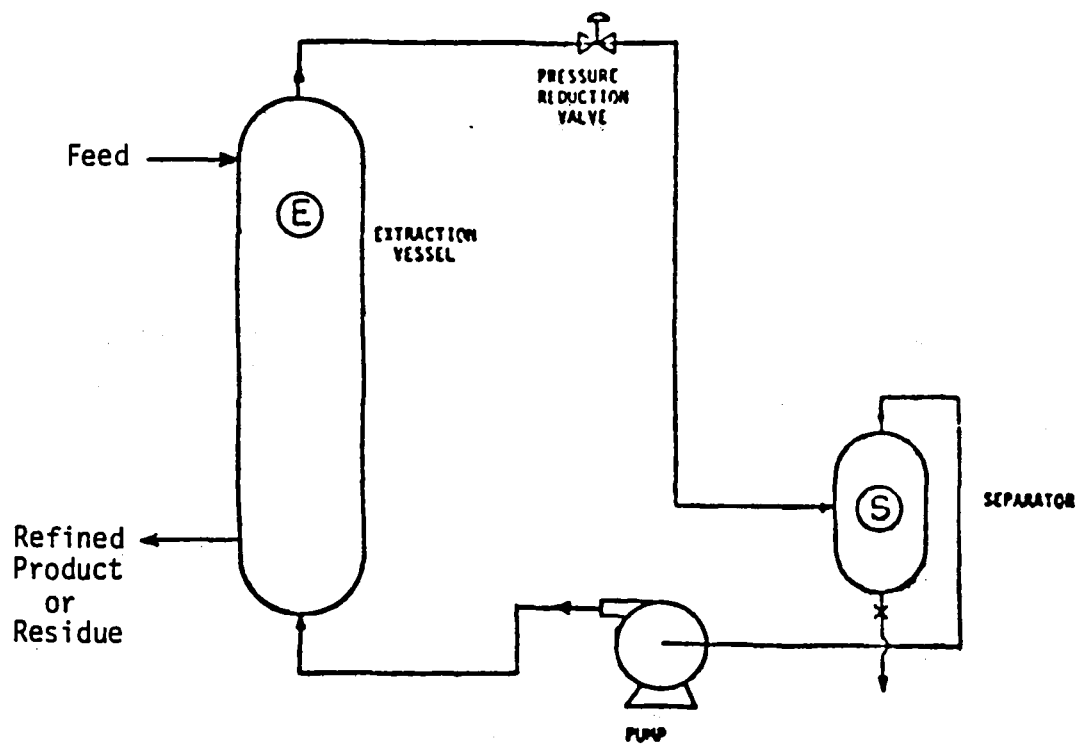


FIGURE 6. SEPARATION BY SOLUBILITY CHANGE

This process arrangement takes advantage of significant changes in solute solubility with temperature and pressure, and requires no vaporization of the solvent. If the pressure and/or temperature swing between extractor and separator conditions are not extreme, the energy requirement for recompressing or heating/cooling of the solvent can be quite small. Also, the energy requirements are directly linked to the quantity of solvent that must be circulated per unit of product produced, be it extract or residue. If the condition change is primarily a pressure swing, the fractional pressure reduction may be relatively small (perhaps $1/3$ or $1/2$ of the extractor pressure), and thus the recompression of solvent may have energy requirements comparable to those required for pumping a relatively incompressible, high-density liquid. This is obviously a favorable circumstance.

The second general case is illustrated in the schematic shown in Figure 7, where solvent-solute separation takes place by vaporization of the solvent. Again, solvent is recirculated through the extractor and separator units, but in this case the separator is an evaporation or distillation unit. The distillation is carried out because the change in pressure and temperature does not bring sufficient solubility change to allow a complete separation, and it is necessary to vaporize the solvent to obtain a recycle stream of adequate purity. Typically, the extractor will operate at pressures above the distillation unit. The distillation unit must, of course, operate at a pressure below the critical pressure in order to allow solvent vaporization.

In this case, energy requirements may still be quite low, because of the high relative volatility of the normally gaseous solvent over the extracted solute, and because the latent heat of vaporization for all fluids becomes greatly reduced as the temperature and pressure approach the critical point.

In both cases, one may make a qualitative comparison with two major established separation processes: distillation and normal-liquid solvent extraction. Distillation is currently used for separating oxygenated organics from water, where such organic chemicals are manufactured in aqueous systems. Examples include common alcohols such as ethanol, propanols, and butanols, as well as high-volume solvents such as methyl ethyl ketone. Other examples include heavy, high-boiling liquids which must be distilled under high vacuum to achieve reasonable temperatures for vaporization. In both classes of examples, distillation energy requirements are substantial. In normal-liquid solvent extraction, the extraction unit per se has minimal energy requirements. However, there is a need to separate solvent from extracted solute, and this is generally done by distillation. Such distillations normally require vaporization of the entire solvent volume, with low relative volatility and high heat of vaporization.

Several additional benefits arise from the favorable kinetic properties of critical fluids as solvents. These have a minor impact on energy requirements, but may be important factors in improving process economics.

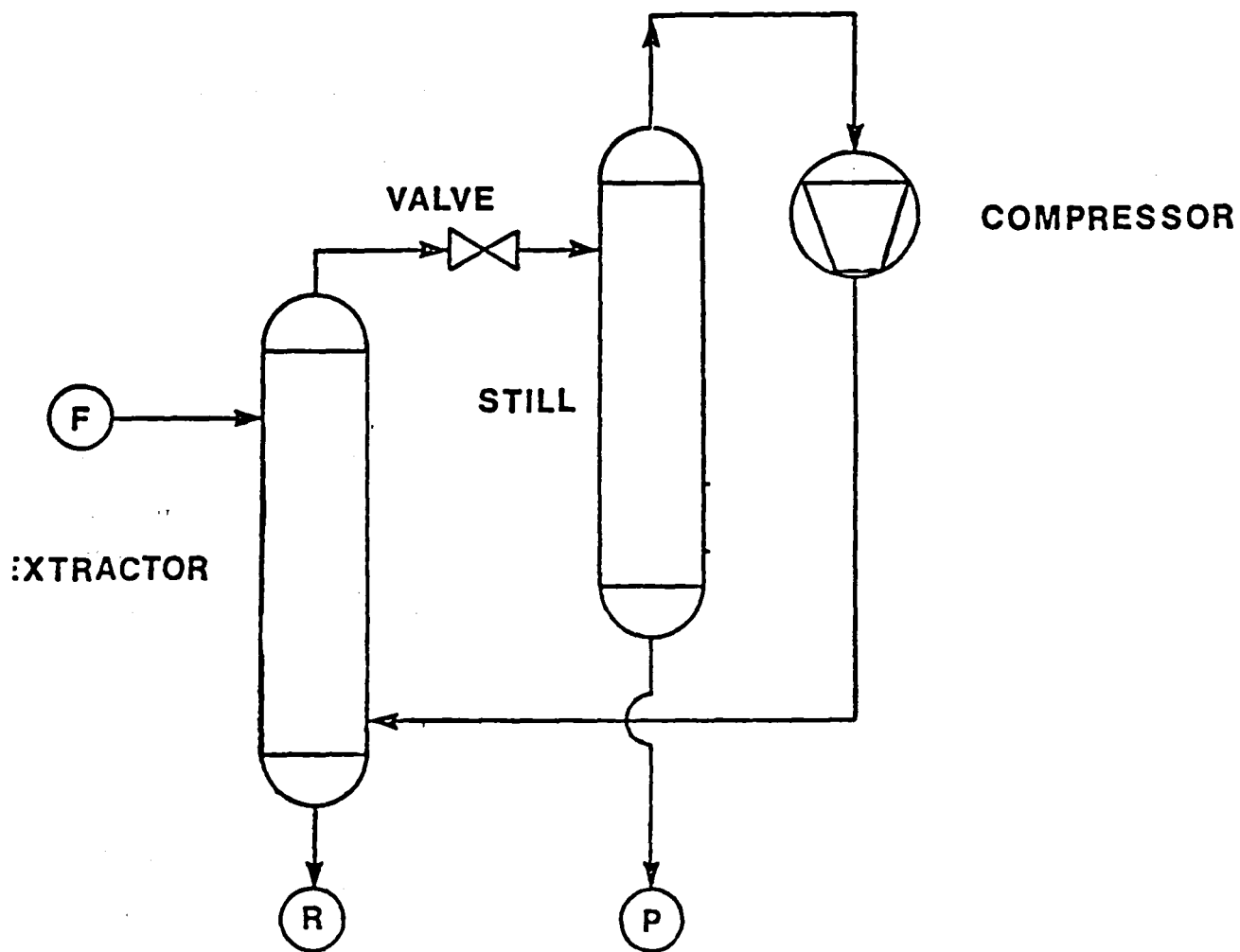


FIGURE 7. SEPARATION BY VAPORIZATION

(For example, the low viscosities of the solvent streams reduce pressure drops, and thus pumping requirements; in general, such pumping energy requirements are small compared to the separation energy needs for the overall process.) Improved diffusion characteristics can lead to higher separation efficiencies in mass transfer equipment, often reducing the volume of such equipment, and thus helping compensate for the higher cost of pressure vessels needed in such extractions.

IV. IDENTIFICATION OF CANDIDATE APPLICATIONS

As a result of a survey of the literature and interviews with commercial and academic groups active in the critical-fluid extraction field, a wide range of applications are apparent. These can be broadly categorized as follows:

1. in commercial use;
2. currently in research and development stages;
3. suggested, without information concerning technical or economic feasibility.

This section contains descriptions of nine applications chosen from these groups as follows. First, those applications currently in commercial use are all included. Second, those applications known to be in research and development stages by commercial organizations interested in using or offering processes are also included. Among those applications in the third category, one has been selected for further consideration based on a preliminary evaluation.

A. Commercial Applications

1. Residual Oil Supercritical Extraction (ROSE) Process

The Kerr-McGee Refining Corporation has developed a supercritical extraction process to convert petroleum vacuum residuum to asphaltenes, resins, and oil (13, 14). The process originally was operated commercially at the Kerr-McGee refinery in Wynnewood, Oklahoma, in the late 1950s at a capacity of 750 barrels per day. A 2700-barrel per day unit to produce lubricating oils and resins has been in operation since 1979, and a 3200-barrel per day unit was scheduled for startup in 1981.

The process utilizes pentane as a solvent, and the company claims that propane, normal butane, isobutane, and other hydrocarbons may also be used. Two important characteristics of the process are its reduced energy costs due to utilization of the supercritical solvent, and the flexibility in designing for different product yields, depending upon petroleum refining requirements.

2. Coffee Decaffeination

A commercial process for removing caffeine from green coffee beans has been in commercial operation by Hag AG (a unit of General Foods) in Bremen, West Germany, for about three years. The process was developed and commercialized under license from Studiengesellschaft Kohle of Mulheim, West Germany (15).

The process utilizes supercritical carbon dioxide at extraction conditions of 120 atmospheres and 40°C. Cleaned, moisturized coffee beans are extracted to a caffeine level of about 0.1%. Supercritical CO₂ is recirculated through the extractor and then into an activated carbon bed, without change in temperature and pressure, for adsorption of the extracted caffeine. The carbon bed effluent is then recycled to the extractor. Solids are charged and discharged in batch operation.

The Bremen plant is reported to be the only commercial operation of this kind at present.

3. Hops Extraction

In the beer brewing industry, there is some incentive to carry out fermentation with a hops extract, rather than using whole hops, although the latter is still common. Hops extract allows for the preservation of the raw material over a longer brewing season and, if properly extracted, can provide a higher quality raw material.

Two variants of processes based on critical carbon dioxide are now being offered commercially. One, offered for license by the Brewers Research Foundation, London, uses liquid carbon dioxide. A commercial operation was started up several months ago at Pauls and Whites Brewery in Reigate, UK (16); a second plant is reported to be in operation in Australia.

The second variant on hops extraction utilizes supercritical carbon dioxide, in a process offered for license by Studiengesellschaft Kohle of Mulheim, West Germany. A plant utilizing this technology is under construction at SKW AG, Trostberg, West Germany (17). Startup is scheduled for late 1982.

B. Processes in Research and Development Stages

1. Separation of Oxygenated Organics From Water

Oxygenated organics such as alcohols, ketones, and carboxylic acids can be extracted from aqueous solutions using carbon dioxide and other critical-fluid solvents. These chemicals are currently produced synthetically in large volume, although some, such as ethanol and n-butanol, are also produced microbiologically. There is a significant possibility that future production may shift to microbiological processes, both through the development of new enzyme catalysts via genetic engineering, and the possibility of carbohydrates becoming a lower-cost and more

readily available raw material than petroleum. The product recovery problem becomes more acute in microbiological processes, because typically product separation must be from a more dilute aqueous stream.

Critical-fluid extraction is currently in pilot-plant testing at Critical Fluid Systems, Inc., Cambridge, Massachusetts, under support from the Department of Energy. The process operates as a liquid-liquid or supercritical fluid-liquid extraction, with product recovered from the critical fluid extract stream by distillation or evaporation (18). That latter step is less energy intensive than the corresponding distillation from the aqueous stream. Economics are determined by the distribution coefficient of organic solute between the solvent and aqueous phase: the higher the distribution of solute into the solvent phase, the better the economics.

2. Lubricating Oil Re-Refining

Development work is currently underway for refining spent lubricating oils, using propane as solvent. This work is being carried out at the Krupp Research Institute in Essen, West Germany (19). Pilot-plant testing is underway.

3. Vegetable Oil Extraction

Vegetable oils, such as soybean, cottonseed, peanut, and corn, are derived from oil seeds by mechanical expression and/or solvent extraction. Usually, mechanical expression by extrusion leaves too high a level of residual oil for discard, and solvent extraction is required to obtain acceptable recoveries. Current solvent extraction technology involves the use of hexane or methylene chloride as solvents.

Bench-scale work is underway for evaluating the use of critical fluids as substitutes for liquids in the extraction step, either for production of the entire oil yield, or the residual after expression. The Northern Regional Laboratory of the U.S. Department of Agriculture has reported work utilizing carbon dioxide at pressures on the order of 350 atmospheres (20). Critical Fluid Systems, Inc., is also carrying out development work with different solvents.

4. Heavy Fossil-Fuels Liquefaction

A major development program was undertaken by the British National Coal Board (21) for coal liquefaction using supercritical toluene and other naphtha boiling-range materials as solvents. Little information has been reported recently, and there are no known large-scale applications. Some research work with shale and peat extraction has been initiated, but no recent results have been described publicly.

5. Regeneration of Adsorbents

Adsorbents, such as activated carbon, used for recovery or removal of dissolved organics from water or vapor-stream purification, require

regeneration and reuse to make the process economical. Various thermal methods are currently used; their major drawback is high energy consumption.

Supercritical carbon dioxide has been tested successfully at the bench scale to regenerate activated carbon and other adsorbents (4). Its advantages include reduced energy requirement, and zero solvent residue after regeneration. The process is being offered for license by Critical Fluid Systems, Inc., both directly and through its licensee Illinois Water Treatment, Rockford Illinois, a unit of Allegheny Ludlum.

6. Extraction of Essences, Flavors, Specialty Chemicals

A fairly wide range of materials have been tested, typically with supercritical carbon dioxide, for improved extraction processes or product qualities. These include essential oils such as lemon, pepper, and lilac; certain pharmaceutical products obtained from fermentation; and specialty chemicals with volatilities too low to be considered for distillation (22). Characteristically, production volumes are small.

Bench-scale tests of extraction of nicotine with carbon dioxide and nitrous oxide have been reported (23), but these do not appear to have advanced beyond that stage.

C. Proposed Applications: Chemical Reaction Systems

Several academic groups have indicated an interest in exploring the advantages of carrying out chemical reactions with solvents in the supercritical state. Little work has been described in this area, although it should be noted that high pressure polyethylene synthesis is carried out under conditions well beyond the critical point of ethylene.

It has been suggested that there may be significant advantages associated with both chemical and mass transfer kinetics in supercritical reactions. In this regime, reasonably high concentrations of reactants could be used, but the lower densities of supercritical fluids, in contrast to normal liquid solvents, may lead to improved chemical kinetics, as well as high diffusion rates either in homogeneous or heterogeneous catalysis. There are no known specific proposals for systems that might be particularly favorable, but the general advantages would seem to make this an interesting area to consider for future research. While operation would be at elevated pressures, improved kinetics at higher concentrations may reduce the energy requirement for product recovery, often the major energy component in chemical reaction systems.

V. ENERGY-PRODUCTIVITY POTENTIAL

Each of the applications described above has been considered for improvement in productive use of energy. There appear to emerge three specific areas that would show strong potential:

1. recovery of oxygenated organics from water;
2. residual oil supercritical extraction;
3. vegetable oil extraction.

An evaluation of each of these is described in this Section.

By way of summary, these applications and their extensions, as well as unexplored areas such as chemical reactions, appear to have a great potential to improve energy productivity. Selection of these three cases by no means eliminates the strong possibility of multiplying the productivity potential well beyond that outlined below. Indeed, that potential is high, and represents a major incentive for the support of long-term research and development in this field.

A. Oxygenated Organics-Water and Other Distillations

In the chemical process industries, distillation is probably the most widely practiced separation process for recovering and purifying products after chemical syntheses. Its predominant place is in the petroleum refining and chemicals manufacturing industries.

Among the highest energy-consuming distillations are water-oxygenated organics. Typically, compounds such as alcohols, ketones, and aldehydes are synthesized in aqueous solution, and require separation from the water solvent by distillation. Many of the product chemicals have high heats of vaporization, or, when less volatile than water, require the evaporation of water for their purification. Also, many of these chemical systems form azeotropes, which further complicate the distillation operation, add to the capital investment, and increase the energy requirement for separation and purification.

Table III summarizes the highest energy-consuming separations among water-oxygenated organics (24). As indicated, the total distillation energy requirement for the chemicals listed is about 0.1 quad* per year. In addition, other unlisted distillations of this kind may raise this total to about 0.14 quad per year.

The specific energy consumption for critical-fluid extraction of an organic from water varies widely, depending upon the physical properties of the system. For example, using carbon dioxide as a solvent, the energy consumption for ethanol separation would be on the order of 1000-1500 Btu per pound. For higher molecular-weight organics, and for carbonyls, this energy consumption is greatly reduced. Comparing these levels with the specific energy consumptions shown in Table II, it is clear that a major proportion of the distillation energy would be eliminated with the successful use of critical-fluid extraction.

In addition to water-oxygenated organics, distillation is used in the fractionation of hydrocarbons in the petroleum industry, separation of

* 1 quad = 10^{15} btu

TABLE 3

WATER-OXYGENATED ORGANICS DISTILLATION ENERGY CONSUMPTION

<u>Component</u>	<u>Total U.S. Distillation Energy Consumption, quads/yr.</u>	<u>Specific Distillation Energy Consumption, Btu/lb. product</u>
Ethylene Glycols	0.01065	2,795
Ethanol	0.01063	9,008
Phenol	0.00947	4,344
Adipic Acid	0.00739	4,862
Methanol	0.00733	1,175
Vinyl Acetate (monomer)	0.00710	4,797
Acetic Acid	0.00701	2,885
Isopropanol	0.00651	3,785
Ethylene Oxide	0.00554	1,325
Methyl Ethyl Ketone	0.00481	9,431
Terephthalic Acid	0.00425	1,756
Acetone	0.00417	2,172
Dimethyl Terephthalate	0.00412	1,567
Formaldehyde	0.00412	733
Acetic Anhydride	0.00267	1,669
Propylene Oxide	0.00219	1,217
Glycerine	0.00202	14,870
Acetaldehyde	0.00174	1,081
Total	0.10172	2,366

light hydrocarbons and aromatics, plus purification of inorganics. The total U.S. distillation energy consumption was estimated in 1978 to be about 1.4 quad per year (24). This represents a significant percentage of the total of 20.1 quads per year (25) consumed by all manufacturing industries in the United States. The extent to which critical-fluid extraction may penetrate these distillation applications remains to be tested by further research.

An additional scenario for growth of critical-fluid extraction as a distillation substitution is related to the increased use of ethanol as a motor fuel additive. One estimate (25) is that energy savings between 0.5 and 0.8 quad per year could be realized in the year 2000 if 24-42 billion gallons of ethanol are used in motor fuels. This scenario involves the use of CO₂ as the critical-fluid solvent. In the event that an improved, higher-selectivity solvent were to result from research and development, the savings could be increased to 0.6-1.0 quads per year by the year 2000.

In summary, use of critical-fluid extraction for separation of oxygenated organics from their aqueous solutions has the potential for saving 0.14 quads per year, based on 1978 figures. The total distillation energy consumption in the chemical process industries is on the order of 1.4 quads per year, which is about 7% of all energy consumed in manufacturing in the U.S. Further, the introduction of ethanol as a motor fuel, if production employed critical-fluid extraction, would realize a savings on the order of 0.5-1.0 quads per year relative to distillation separation technology, in the year 2000.

B. Residual Oil Supercritical Extraction

The successful introduction of residual oil supercritical extraction (ROSE) apparently comes as a direct result of the reduced energy consumption compared to established residual-oil-to-asphalt processes. Recent publications (13, 14) provide detailed energy requirements of the ROSE process compared to propane deasphalting, and these are summarized in Table IV. The net energy reduction is about 250,000 Btu (fossil fuel) per barrel of residuum feed.

In 1979, 167 million barrels of asphalt were produced in the U.S. (26). The yield of asphalt from the ROSE process is about 20%. Thus, to generate the 1979 asphalt production level entirely from this process, 835 million barrels of resid per year would be processed. Multiplying this level by the energy reduction per barrel gives 0.21 quad per year of energy reduction.

It is evident from Table III that still further energy reductions may be possible with further process research; however, one must be cognizant of the minimum thermodynamic energy requirement for the separation. There is insufficient data from the literature to determine the latter, although it is generally true that actual operating energy requirements far exceed such minimums.

TABLE 4
ENERGY SAVINGS THROUGH
RESIDUAL OIL SUPERCRITICAL EXTRACTION (ROSE)
(Per Barrel of Residuum Feed)

	<u>Propane Deasphalting</u>	<u>ROSE</u>	<u>Δ</u>	<u>Δ, as Btu Fossil Fuel</u>
Power, kwh	2.8	2.7	0.1	1,050 ⁽¹⁾
Steam, lbs	215	10	205	256,250 ⁽²⁾
Fuel, M BTU	137	143	-6	-6,000
			NET	<hr/> 251,300

(1) 10,500 Btu fossil fuel per kwh.

(2) 1,250 Btu fossil fuel per pound of steam.

It is also worth noting that the successful energy reduction brought about by improved extraction technology in fractionating residual oil may indicate promise for application of critical-fluid extraction to other aspects of petroleum refining; about 0.8 quad per year is currently used in petroleum refining distillation (24).

C. Extraction of Vegetable Oils

Vegetable oilseeds are currently processed into oil and meal fractions, with oil production going into margarine and cooking oils. Extraction processes differ, depending on the specific oilseed, but solvent extraction with hexane is a predominant process technology. Hexane is recovered from the oil extract by distillation.

In 1980, about 15 billion pounds of vegetable oil were produced in the U.S., predominantly soybean (27). An estimate of the total energy requirement can be made by focusing solely on the distillation to recover hexane from extract, typically a 20% oil-in-hexane solution. Thus, 4 pounds of hexane are distilled per pound of oil produced. The latent heat of hexane is about 150 Btu per pound, and reflux requirements in the fractionation column may raise this to the order of 200 Btu per pound. Multiplication of these figures give an annual energy requirement on the order of 0.01 quads per year for such distillations.

Critical-fluid extraction with CO₂ and other solvents has been studied, and is currently under development. The energy requirement for distilling a critical solvent such as CO₂ would be quite small compared to hexane distillation requirements, particularly if one considers the use of a vapor recompression cycle. Thus, it is possible that most of the energy now required for hexane separation from the extract oil could be potentially conserved with the use of a critical-fluid extraction process.

VI. RESEARCH PRIORITIES

In many respects, research and development on critical-fluid extraction represent the extension of established chemical process technologies into a regime of temperatures, pressures and fluids previously untested for this purpose. That regime has never been fully investigated, and there is a dearth of the usual fundamental information on fluid properties. Only within the last 5-10 years have thermodynamic equations of state been established as reliable prediction tools around the critical point, and little has been done regarding transport properties.

At the same time, there is a substantial need to obtain basic process data on real applications, and this probably should not await clearly-established knowledge of fundamentals.

Finally, it has been recognized that there may be a significant potential value to carrying out chemical syntheses in critical-fluid solvents, but this field remains virtually unexplored.

Thus, while it may be appropriate to list a logical sequence and priority of research studies to be carried out in the field, from a practical viewpoint the field would benefit by the simultaneous emphasis of each of these areas. The following may be considered to be a chronological sequence that would best accelerate understanding and practice of critical-fluid extraction, but is not intended to reduce emphasis on certain areas. These priorities would include:

1. applications data on real systems;
2. studies of transport phenomena and unit operations;
3. thermodynamic data;
4. chemical reactions.

A. Applications Data for Real Systems

To date, there appears to have been a wider range of applied research and development carried out in Europe using supercritical carbon dioxide, compared to more limited work done in the United States. Such work has led to certain initial applications of the technology, such as coffee decaffeination and hops extraction, which have a relatively low impact on energy productivity in a broad sense. However, the R&D experience associated with these developments is instructive. Specifically, it has been recognized that process information on real systems, albeit complex and difficult to analyze, has been of fundamental importance in providing bench- and pilot-scale data from which engineering tradeoff analyses could be made. Characteristically, supercritical CO₂ extractions have been found to produce higher quality products at energy costs that are lower than those of normal liquid extractions or other separation processes. These are achieved with increased capital equipment requirements, because of pressure operation, and by processing more dilute solutions, because of typically lower solubilities of extracts in carbon dioxide compared to hydrocarbon or chlorinated hydrocarbon solvents. Additional benefits of the use of CO₂ come from its nontoxic and nonpolluting nature and low cost.

In any potential application, a range of process conditions must be studied to obtain information sufficient to allow optimization with respect to energy and solvent costs, plus capital equipment requirements. Such systematic information is not publicly available, and should be generated for various broad fields described in previous sections:

1. both synthetic and biosynthetic chemical mixtures, especially those involving aqueous solutions.
2. natural products, including foods such as vegetable oils;
3. fossil fuels, such as petroleum, coal, and possibly tarsands, heavy crudes, and shale.

A second area where applied research is needed, along with fundamental studies that would be helpful in parallel, is that of solvents and solvent mixtures. It is apparent in many cases that pure carbon dioxide or light hydrocarbon gases do not possess adequate selectivity and solvent power for many extractions of interest. Thus, the addition of cosolvents which can improve these properties is required, and they may become the key developments that will push many applications over into economic use.

A third area associated with each application is the engineering evaluation of process systems, involving combinations of unit operations coupled to critical-fluid extractions. For example, in the extraction of ethanol from aqueous solutions, completely dehydrated product will probably not be achievable. However, high alcohol concentrations can be reached, perhaps sufficient to encourage the use of dehydration alternatives to azeotropic distillation, such as mol-sieve adsorption. By the same token, pretreatment of extractor feeds may be worthwhile, to help eliminate complications in the separation that may occur due to the presence of other dissolved or undissolved components, such as in fermentation beers. While it would appear that such evaluations would be appropriately carried out when a process is near commercialization, it is probable that the entire technical and economic feasibility of some of these newer extraction applications may rest on the ability to design coupled process systems. Several operating examples of such systems may be required before industry is prepared to undertake further development and engineering on its own.

B. Transport Phenomena and Unit Design

Critical-fluid extractions may be considered a classical unit operation requiring fundamental information on transport processes and thermodynamics to provide the basis for scale-up from bench-scale and pilot data. Such data is mandatory to enable the design of mass transfer systems, such as countercurrent columns and batch extraction equipment. These data would serve as the basis for correlation of rate coefficients with system properties (temperature, pressure, flows) and fluid properties (transport coefficients such as diffusivity and viscosity, plus thermodynamic properties). At present, these design and correlation practices are well established for gases and liquids. The key question requiring R&D is whether such correlations hold at conditions near the critical point.

To answer this, programs are required to provide:

1. additional transport-property data for different solvents, correlated with temperature and pressure;
2. well-designed bench-scale data to measure transport rates and coefficients in simulations of real geometries (such as packed beds), and tests of existing correlations plus generation of new ones if needed;

3. confirmation of such information at pilot-plant scale.

C. Thermodynamic Data

It is apparent both from public literature and interviews with academic and industrial groups that much work is in progress on generalized equations of state for thermodynamic properties around the critical point. A great deal of progress has been made for single components, and there is current effort ongoing in multiple-component systems. Continuing needs exist along the following lines:

1. more experimental data to provide tests of current theories, particularly with multi-component solutions;
2. greater accuracy within narrow regimes of interest, rather than broad-range approaches which are less accurate;
3. extension of approaches to difficult systems such as polar solutions, particularly aqueous;
4. extension of data bases to solid phases, such as hydrates formed at high pressure.

D. Chemical Reactions

There are no published data available on the effects of carrying out chemical reactions near the critical point, relative to liquid or gas-phases, in either catalyzed or uncatalyzed systems. At this stage, such studies must of necessity be purely exploratory. Fundamental questions that require answers concern the possibilities of kinetic and chemical mechanism changes that may occur in this regime, with fluids acting as a low-density liquid solvent.

While the uncertainty in this area is great, the potential payoff for many chemical syntheses could be very significant. The consequences of improvements in chemical-reaction systems would include production of more concentrated products, and reduced reactor volumes, both of which have substantial implications for energy productivity. Studies of both homogeneous and heterogeneous catalysis in this regime would be of great interest.

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APPENDIX A

STATEMENT OF WORK

ARTICLE 1. STATEMENT OF WORK

- (a) The Contractor shall conduct a study of candidate applications for critical-fluid extractions in the process industries and define research necessary to overcome technological obstacles. Emphasis shall be on high risk applications areas. In accomplishing this study, the Contractor shall:

(1) Task 1 - Identification of Candidate Applications

- (A) Conduct interviews in Europe and the United States with academic and industrial organizations currently researching critical-fluid extractions.
- (B) List candidate applications which have a high payoff potential, based upon information obtained from interviews and other non-proprietary sources.
- (C) Define research necessary for the selected candidate applications.

(2) Task 2 - Estimation of Energy Savings Potential

Provide preliminary estimates of the energy consumption per unit of product manufactured in each candidate process, based upon the Contractor's existing quantitative correlations and analysis of the physical properties of the chemical systems involved. The quantitative data will be combined with data on process capacities to give estimates of the potential impact of critical-fluid extraction technology on national energy conservation.

(3) Task 3 - Documentation and Briefing

- (A) Provide one (1) reproducible and five (5) copies of a brief Monthly Progress Report which is technically oriented in narrative form and shall include, but not necessarily be limited to, a schedule to describe progress, significant results and conclusions, problems encountered and how resolved, and a projection of activities to occur.
- (B) Provide one (1) reproducible and three (3) copies of a draft Final Report for review and comment by JPL.
- (C) The Contractor shall incorporate the JPL review comments and required revisions and shall provide one (1) reproducible and ten (10) copies of an approved Final Report. The Final Report shall consist of, but not necessarily be limited to, and discussion of the findings from the entire study effort.

APPENDIX B
LIST OF INTERVIEWEES

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